

The Third Order Elastic Constants Of NaCl and KCl Single Crystals

NSG-100

Zung-Ping Chang

UNPUBLISHED PRELIMINARY DATA

Department of Physics, Rensselaer Polytechnic Institute Troy, New York

^{*} Supported by the National Aeronautics and Space Administration, and by the National Science Foundation

The Third Order Elastic Constants Of NaCl and KCl Single Crystals+#

Zung-Ping Chang*
Department of Physics, Rensselaer Polytechnic Institute
Troy, New York

ABSTRACT

23196 OVER

Measurements have been made to determine the third order elastic constants of NaCl and KCl single crystals. The relations between the velocities of ultrasonic waves propagating along the [1 $\overline{10}$] and [$\overline{11}$ 2] directions under a uniaxial compression applied in the [111] direction and the elastic constants were derived. Six velocities of these ultrasonic waves were then measured at room temperature as functions of the strain using the pulsed ultrasonic interference technique. From the present measurements under the .111 > compression and those under the hydrostatic pressure by Lazarus, eleven equations were obtained for both NaCl and KCl crystals. From these equations, the following five constants (Brugger's definition for the third order elastic constants) in units of 10^{12} dynes/cm² were solved by the method of least squares:

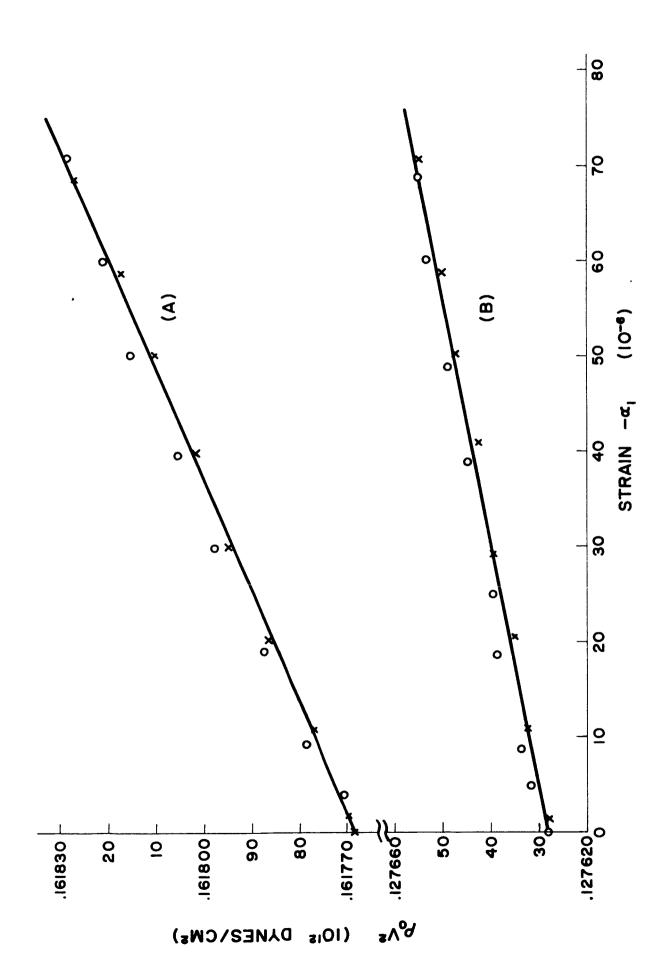
$$\frac{C_{111}+2C_{112}}{C_{111}-C_{123}} \quad \frac{C_{456}}{C_{456}} \quad \frac{C_{144}}{C_{166}}$$
NaCl -9.91 \pm .04 -9.10 \pm .08 .271 \pm .014 .257 \pm .016 -.611 \pm .007
KCl -7.44 \pm .01 -7.15 \pm .02 .118 \pm .004 .127 \pm .005 -.245 \pm .002

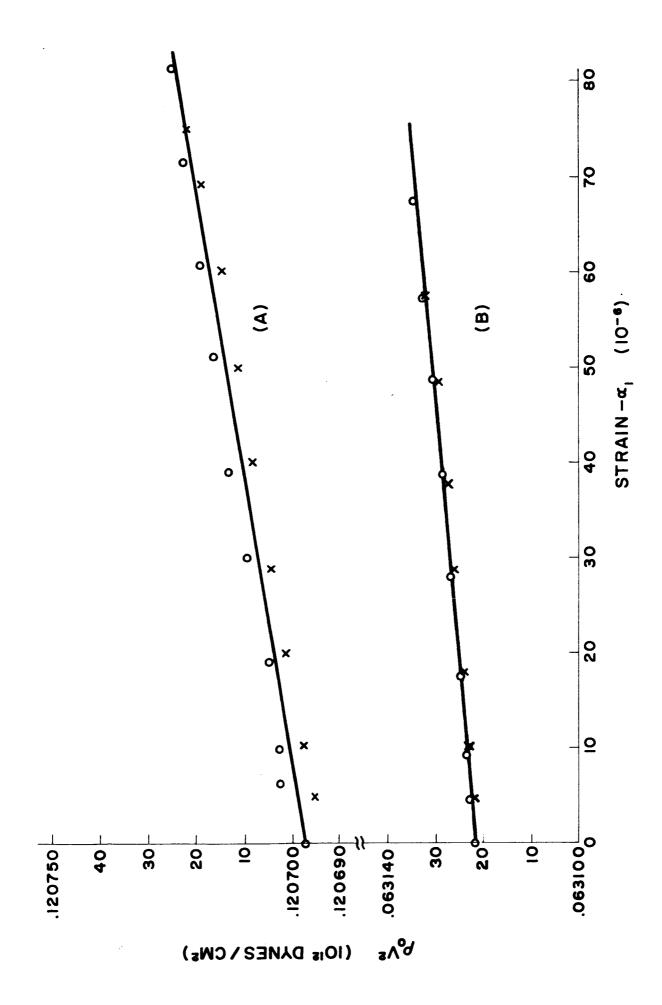
The Cauchy relation $C_{456}^{=}C_{144}^{}$ is seen to be satisfied to within the

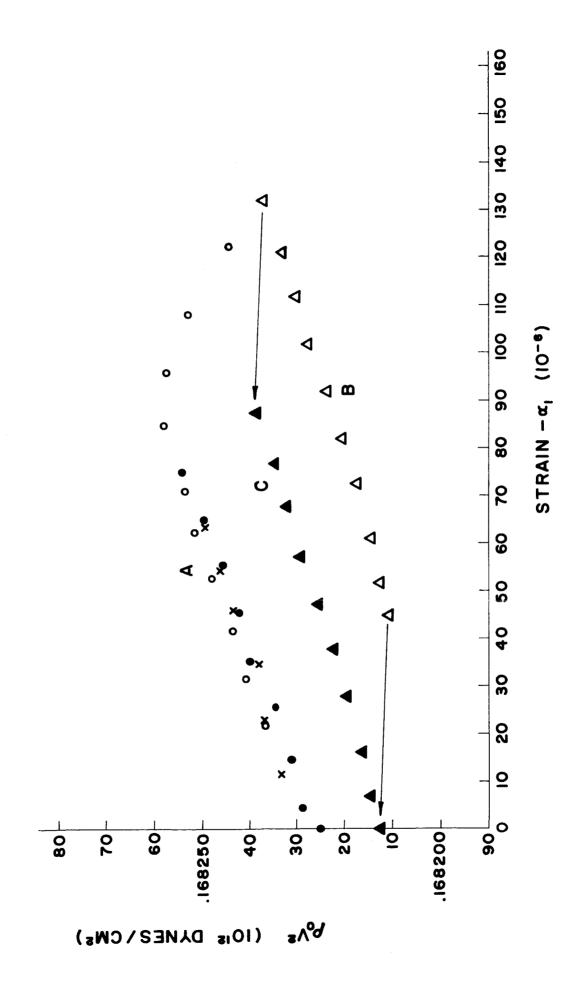
⁺ This work is based on a portion of a thesis submitted in partial fulfillment of the requirements for the Ph.D. degree.at Rensselaer Polytechnic Institute, 1964.

[#] Supported by the National Aeronautics and Space Administration, and by the National Science Foundation.

^{*}Present address: Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania.







probable error in both NaCl and KCl crystals at room temperature. By assuming the validity of the other two Cauchy relations, one can estimate the constants $^{\rm C}_{111}$, $^{\rm C}_{112}$ and $^{\rm C}_{123}$ as follows:

	<u>C</u> 111	^C 112	C ₁₂₃
NaC1	-8.80	571	.248
KC1	-7.01	224	. 113

I. INTRODUCTION

The third order elastic constants are quantities of interest because they relate to the anharmonic properties of the crystal lattices. Their values determine in the long wavelength limit the phonon-phonon coupling which limits the thermal relaxation time. They also contribute to the thermal expansion and to the lattice specific heat at temperatures higher than the Debye characteristic temperature. They are manifest in the non-linear properties of sound waves in a solid, e.g., the second harmonic generation the intersection of two sound beams to generate a third beam and the asymmetry in the diffraction pattern formed by passing nomochromatic light through a cubic crystal perpendicular to the direction of a sound wave.

In determining the third order elastic constants, we have chosen the direct method of observing the change of sound velocity in a solid under compression. Accurate velocity measurement is necessary since the velocity change is usually small in the available pressure range. The introduction of an interference method enables the detection of quite small changes in the velocity and opens the way for the measurement of the third order elastic constants.

So far the variation of sound velocity with stress has mostly been measured under hydrostatic pressure. In order to obtain the complete set of the third order elastic constants of a material, other conditions of stress, such as uniaxial compression, have to be applied. The difficulty lies in that even a low uniaxial stress can initiate slip and plastic deformation, and the dislocations generated by such flow will cause large

Up to the present, very few measurements have been made to determine the whole set of the third order elastic constants. The first measurement was made by Hughes and Kelly (1953) who determined the three independent third order elastic constants of the isotropic materials: polystyrene, Pyrex, and Armco iron. In 1961, Bateman, Mason, and Mc8kimin determined the six independent third order elastic constants of germanium, a first experiment of this kind on a cubic material.

Alkali halides are substances of interest from the theoretical point of view because a simple model of their structure has been quite successful. No complete determination of their six independent third order elastic constants has yet been made. The variation of elastic constants has, however, been measured by Lazarus (1949) and Bartels (1964).

Although there are many easy slip systems in NaCl-type alkali halides, it turns out that the resolved shear stress in the primary easy slip directions, $\langle 110 \rangle$ in the slip planes $\{1\overline{1}0\}$, are zero for uniaxial stress applied in a [111] direction. For this orientation of stress the elastic range in which one can make measurements without yielding is considerably extended.

II. THEORY

In the present paper Brugger's definition of the third order elastic constants is used. With his definition, the strain energy ¢ in a cubic lattice can be expressed in terms of the strain components as:

$$\phi = \frac{1}{2} \; C_{11} \; \left(\begin{smallmatrix} 2 \\ \eta_{11} + \eta_{22} + \begin{smallmatrix} 2 \\ \eta_{33} \end{smallmatrix} \right) + C_{12} \; \left(\begin{smallmatrix} \eta_{11} & \eta_{22} + \eta_{22} & \eta_{33} + \eta_{33} & \eta_{11} \end{smallmatrix} \right)$$

$$+ C_{44} \left(n_{12}^{2} + n_{21}^{2} + n_{23}^{2} + n_{32}^{2} + n_{31}^{2} + n_{13}^{2} \right) + \frac{1}{6} C_{111} \left(n_{11}^{3} + n_{22}^{2} + n_{33}^{3} \right)$$

$$+ \frac{1}{2} C_{112} \left\{ n_{11}^{2} \left(n_{22}^{2} + n_{33} \right) + n_{22}^{2} \left(n_{33}^{3} + n_{11} \right) + n_{33}^{2} \left(n_{11}^{2} + n_{22} \right) \right\}$$

$$+ C_{123} n_{11} n_{22} n_{33} + C_{456} \left(n_{12}^{2} + n_{21} \right) \left(n_{23}^{2} + n_{32} \right) \left(n_{31}^{3} + n_{13} \right)$$

$$+ C_{144} \left\{ n_{11} \left(n_{23}^{2} + n_{32}^{2} \right) + n_{22} \left(n_{13}^{3} + n_{31}^{3} \right) + n_{33} \left(n_{12}^{2} + n_{21}^{2} \right) \right\}$$

$$+ C_{166} \left\{ \left(n_{11}^{2} + n_{22}^{2} \right) \left(n_{12}^{2} + n_{21}^{2} \right) + \left(n_{22}^{2} + n_{33} \right) \left(n_{23}^{2} + n_{32}^{2} \right) + \right.$$

$$+ \left. \left(n_{33}^{3} + n_{11} \right) \left(n_{31}^{2} + n_{13}^{2} \right) \right\}$$

$$(1)$$

where η_{ij} are the components of the Lagrangian strain which are defined in the following matrix equation 10 :

$$[\eta] = \frac{1}{2} \left[J \stackrel{\sim}{J} - E \right] \tag{2}$$

Here J is the Jacobian relating the final position of a particle in the lattice after deformation and its initial position, and E is a unit matrix of rank 3.

For the convenience of comparison with the expressions in other literatures, the relations between the C_{ijk} defined by Brugger (C_{ijk}^{Br}) and by Eirch 9 (C_{ijk}^{Bi}) are listed below:

$$\begin{array}{l} c_{111}^{Br} = 6c_{111}^{Bi} \; , \; c_{112}^{Br} = 2c_{112}^{Bi} \; , \; c_{123}^{Br} = c_{123}^{Bi} \\ c_{456}^{Br} = \frac{1}{4} \; c_{456}^{Bi} \; , \; c_{144}^{Br} = \frac{1}{2} \; c_{144}^{Bi} \; , \; c_{166}^{Br} = \frac{1}{2} \; c_{166}^{Bi} \end{array}$$

^{(*} The relation between Birch's C_{456} and Brugger's C_{456} should be $C_{456}^{Br} = \frac{1}{4} C_{456}^{Bi}$, not $\frac{1}{8}$ as obtained from eq.(13) in Brugger's paper⁸, if the C_{456} term in the expression of the strain energy is C_{456} ($\eta_{12}\eta_{23}\eta_{31} + \eta_{21}\eta_{32}\eta_{13}$) as it is in Birch's paper⁹.

For the stress applied in the [111] crystallographic direction, it is easier to transform the calculation in a new coordinate system with the 1', 2' and 3' -axes in the [111], [1 $\overline{1}$ 0] and [$\overline{1}$ 12] directions respectively. Hereafter a single prime will be used to denote the quantities referred to the new coordinate system. The transform matrix [R] relating these two coordinate systems by the matrix equation

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} R \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

is found to be

$$[R] = \begin{bmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{2}{\sqrt{6}} \end{bmatrix}$$
(3)

The relation between the strains in the two coordinate system is

$$[n] = [R] [n'] [R]$$
 or $[n'] = [R] [n] [R]$ (4)

As in Birch's analysis⁹, let us consider a deformation in which the final position (x'_1, x'_2, x'_3) of a particle initially at (a'_1, a'_2, a'_3) is given by

$$[x'] = [A'] [a'] + [U'(a', t)]$$
 (5)

where [x'], [a'], and [U'(a', t)] are column vectors standing respectively for the final, the initial position, and an infinitesimal displacement which is a general function of the initial position a' and the time t, and [A'] is a 3×3 matrix describing a finite homogeneous deformation due to an initial stress. From (5), the Jacobian

$$\frac{\delta(x'_1, x'_2, x'_3)}{\delta(a'_1, a'_2, a'_3)}$$

and hence the Lagrangian strain η can be calculated.

If one takes into account the fact that the three cubic axes are equivalent with respect to the [111] direction, then for a uniaxial stress in the [111] direction, the suffixes 1, a and 3 in η_{ij} are interchangeable, i.e., $\eta_{11} = \eta_{22} = \eta_{33}$ and $\eta_{12} = \eta_{23} = \eta_{31}$, and from (4) one can show $\eta_{11}^i = \eta_{11} + 2\eta_{12}, \ \eta_{22}^i = \eta_1^i = \eta_1 - \eta_1 \text{ and } \eta_1^i = \eta_1^i = \eta_1^i = 0. \text{ Hence the } 1^i, 2^i \text{ and } 3^i - \text{axes form a set of principal axes with the strain being isotropic in the plane normal to 1' - axis, and thus the matrix A' is diagonal with <math>A_1^i = A_1^i$. The Lagrangian strain η_1^i resulting from this initial uniaxial stress are

$$\eta_{11}^{\prime (0)} = \frac{1}{2} (A_{11}^{\prime 2} - 1) \equiv \alpha_{1}$$

$$\eta_{22}^{\prime (0)} = \eta_{33}^{\prime (0)} = \frac{1}{2} (A_{22}^{\prime 2} - 1) \equiv \alpha_{2}$$

$$\eta_{1}^{\prime (0)} = 0 \text{ for } i \neq j$$
(6)

In the finite deformation theory, the stress and the strain are related by $^{10}\,$

$$[T'] = \frac{\rho_{\mathbf{x}}}{\rho_{\mathbf{o}}} [J'] \left[\frac{\delta \phi(\eta(\eta'))}{\delta \eta'} \right] [J']$$
 (7)

where [T'] is the stress tensor, ρ_{0} and ρ_{x} are the initial and the final density respectively.

For an initial stress -t (t positive for compression) in the [111] direction, the stress tensor $[T^{\dagger}]$ is

The values α_1 and α_2 of the Lagrangian strain $\eta^{(0)}$ and $\eta^{(0)}$ can be found from the two linearly independent equations in (7):

$$-\frac{1+2\alpha_2}{\sqrt{1+2\alpha_1}} t = \frac{1}{3} (C_{11} + 2C_{12}) + \frac{4}{3} C_{44} \delta + (\frac{1}{18} C_{111} + \frac{1}{3} C_{112} + \frac{1}{9} C_{123}) \theta^2 + \frac{8}{9} C_{456} \delta^2 + \frac{2}{3} C_{144} \delta (\alpha_1 + \alpha_2) + \frac{4}{3} C_{166} \delta (\alpha_1 + \alpha_2)$$

$$0 = \frac{1}{3} (C_{11} + 2 C_{12}) \theta - \frac{2}{3} C_{44} \delta + (\frac{1}{18} C_{111} + \frac{1}{3} C_{112} + \frac{1}{9} C_{123}) \theta^2 - \frac{4}{9} C_{456} \delta^2 - \frac{2}{3} C_{144} \delta \alpha_2 - \frac{4}{3} C_{166} \delta \alpha_2$$

where $\theta \equiv \alpha_1 + 2\alpha_2$

$$\delta \equiv \alpha_1 - \alpha_2 \tag{8}$$

The Poisson ratio σ for the strain perpendicular to [111] direction with the stress in [111] direction is $-\frac{\alpha_2}{\alpha_1}$ which can be obtained from

(8) by neglecting the second and higher order terms of α_1 . The result is $\sigma = \frac{C_{11} + 2C_{12} - 2C_{44}}{\epsilon - \epsilon}$ $2(C_{11} + 2C_{12} + C_{44})$ (9)

In the last expression, a superscript θ is added to emphasize that isothermal elastic constants should be used for the initial strain, since the process for the initial compression is an isothermal one.

For the infinitesimal part of the deformation [U'] in (5), consider a travelling plane wave with a wave vector \vec{k} .

$$U_{\mathbf{i}}' = \overrightarrow{U}' \cdot \overrightarrow{x}_{\mathbf{i}}' \exp \left[\mathbf{i}(\mathsf{wt} - \overrightarrow{k}' \cdot \overrightarrow{x}')\right] \tag{10}$$

For a plane wave propagating along a general direction, the displacement vector U' may be neither parallel nor normal to the wave vector. From the matrix [A'] and this displacement vector U', one can calculate the Jacobian, the Lagrangian strain η'_{ij} (eq. 2), and the stress tensor [T'] (eq. 7).

Substituting this [T'] into the equations of motion in an elastic medium:

$$\sum_{\mathbf{j}} \frac{\partial \mathbf{T}'_{\mathbf{j}}}{\partial \mathbf{x}'_{\mathbf{j}}} = \rho_{\mathbf{x}} \mathbf{U}'_{\mathbf{j}} \tag{11}$$

and neglecting the second and the higher order of U', one obtains a set of three equations for $U_1^!$, $U_1^!$, and $U_1^!$ which can be written in the following matrix form

$$[H] \begin{bmatrix} U_1^{\dagger} \\ U_2^{\dagger} \\ U_3^{\dagger} \end{bmatrix} = \rho_0 V^2 \begin{bmatrix} U_1^{\dagger} \\ U_2^{\dagger} \\ U_3^{\dagger} \end{bmatrix}$$

$$(12)$$

where V is the phase velocity of a sound wave, and $V^{2} = \frac{\omega}{\left|\frac{1}{k^{2}}\right|^{2}}$

[H] is a 3 x 3 matrix whose elements contain the second and third order elastic constants and the strains α_1 and α_2 .

For small strains one can consider the terms in [H] containing $\alpha_{\bf i}$ (i=1,2) to be the perturbing terms. The problem is then to diagonalize [H] to the zeroth order of $\alpha_{\bf i}$. The calculation is in general quite tedious but much simplified if pure modes exist.

For wave propagating along [1] direction (i.e. 2'-axis) under a uniaxial compression applied in [11] direction (1'-axis), the compressional wave is still a pure mode, since such a wave was originally a pure mode, and under this compression the stress does not alter the displacement of the particle motion. Hence one may consider the following wave motion

$$U'_{2} = B \exp \left[i(wt - k'_{2} x'_{2})\right]$$

$$U'_{1} = U'_{2} = 0$$
(13)

Substituting this into (11), one immediately obtains one of the eigenvalues of $\rho_0^{\ \ 2}$ (second equation in (12)).

The remaining operator which is now a 2 x 2 matrix can easily be diagonalized to the zeroth order of $\alpha_{\bf i}$ by applying a unitary transformation with the unitary transform matrix constructed from the normalized eigenvectors of the unperturbed operator. For small strains such that the second order terms of $\alpha_{\bf i}$ can be neglected in the expression of $\alpha_{\bf i}$ the eigenvalues are readily found from the diagonal terms.

For waves propagating along $[\overline{112}]$ direction the shear wave polarized in $[1\overline{10}]$ direction is still a pure mode under a compression in [111] direction. The calculation resembles that for waves propagating along $[1\overline{10}]$ direction but is much more complicated. The expressions for $\rho_0^{\ \ V}$ are listed below (eqs. 14 - 19). For convenience the expression of $\rho_0^{\ \ \ V}$ under hydrostatic pressure and under [110] compression are also listed (eqs. 20 to 26).

(A) Under uniaxial compression in [111] direction

For compressional wave in [110]

$$\rho_{0}V_{22}^{2} = \frac{1}{2} (C_{11} + C_{12} + 2C_{44}) + \left\{ -2(C_{11} + C_{12} + 2C_{44}) \sigma + \frac{1}{3} (C_{111} + 2C_{112}) (1 - 2\sigma) - \frac{1}{6} (C_{111} - C_{123}) (1 - 2\sigma) + \frac{1}{3} C_{144} (1 - 2\sigma) - \frac{2}{3} C_{166} (1 + 4\sigma) \right\} \alpha_{1}$$
(14)

For shear wave in $[1\overline{1}0]$ polarized in [110]

$$\rho_{o}V_{2ti}^{2} = \frac{1}{2} (c_{11} - c_{12}) + \left\{ \frac{2}{3} (c_{11} - c_{12}) (1 - 2\sigma) + \frac{1}{6} (c_{111} - c_{123}) \right\}$$

$$(1 - 2\sigma) \alpha_{1}$$
(15)

For shear wave in $[1\overline{1}0]$ polarized in [001]

$$\rho_{0}V_{2t2}^{2} = C_{44} = \frac{1}{3} \left\{ 2C_{44} (1 - 5\sigma) - 2 C_{456}(1 + \sigma) + C_{144} (1 - 2\sigma) + 2C_{166} (1 - 2\sigma) \right\} \alpha_{1}$$
(16)

For shear wave in $[\overline{112}]$ polarized in $[\overline{110}]$

$$\rho_{0}V_{32}^{2} = \frac{1}{6} (C_{11} - C_{12} + 4C_{44}) + \left\{ -\frac{2}{3} (C_{11} - C_{12} + 4C_{44}) \sigma + \frac{1}{18} (C_{111} - C_{123}) (1 - 2\sigma) - \frac{4}{9} C_{456} (1 + \sigma) + \frac{2}{3} C_{144} - \frac{4}{3} C_{166} \sigma \right\} \alpha_{1}$$
(17)

For quasi-compressional wave in $[\overline{11}2]$

$$\rho_{0}V_{33}^{2} = \frac{1}{12} \left(5C_{11} + C_{12} + 8C_{44} + R\right) + \left[\frac{2}{3} s_{11}^{2} \left(C_{11} - C_{12} + C_{44}\right) (1 - \sigma)\right]$$

$$- \frac{\sqrt{2}}{3} s_{11} s_{12} \left(C_{11} - C_{12} - 2C_{44}\right) (1 - 3\sigma) - 2s_{12}^{2} \left(C_{11} + C_{12} + 2C_{44}\right) \sigma\right] + 2C_{44}\sigma\right] +$$

$$+\frac{1}{3} s_{12}^{2} (C_{111} + 2C_{112}) (1 - 2\sigma) + (\frac{1}{9} s_{11}^{2} - \frac{\sqrt{2}}{9} s_{11} s_{12} - \frac{1}{6} s_{12}^{2}) (C_{111} - C_{123}) (1 - 2\sigma) + (-\frac{2}{9} s_{11}^{2} - \frac{8}{9\sqrt{2}} s_{11} s_{12}) C_{456} (1 + \sigma) + \\
+ \left[-\frac{1}{3} s_{11}^{2} (1 + 2\sigma) - \frac{4}{3\sqrt{2}} s_{11} s_{12}\sigma + \frac{1}{3} s_{12}^{2} (1 - 2\sigma) \right] C_{144} + \\
+ \left[\frac{2}{3} s_{11}^{2} + \frac{4}{3\sqrt{2}} s_{11} s_{12} (1 - \sigma) - \frac{2}{3} s_{12}^{2} (1 + 4\sigma) \right] C_{166} \qquad \alpha_{1} \qquad (18)$$

For quasi-shear wave in [112] polarized in [111]

$$\rho_{0}V_{31}^{2} = \frac{1}{12} \left(5C_{11} + C_{12} + 8C_{44} - R\right) + \left\{ \left[\frac{2}{3} s_{12}^{2} (C_{11} - C_{12} + C_{44}) (1 - \sigma) \right. \right. \\
+ \frac{\sqrt{2}}{3} s_{11} s_{12} (C_{11} - C_{12} - 2C_{44}) (1 - 3\sigma) - 2s_{11}^{2} (C_{11} + C_{12} + 2C_{44}) \sigma \right] + \frac{1}{3} s_{11}^{2} \left(C_{111} + 2C_{112} \right) (1 - 2\sigma) + \left(\frac{1}{9} s_{12}^{2} + \frac{\sqrt{2}}{9} s_{11} s_{12} - \frac{1}{6} s_{11}^{2} \right) (C_{111} - C_{123}) (1 - 2\sigma) + \left(\frac{2}{9} s_{12}^{2} + \frac{8}{9\sqrt{2}} s_{11} s_{12} \right) C_{456} \left(1 + \sigma \right) + \left. \left. \left(-\frac{1}{3} s_{12}^{2} (1 + 2\sigma) + \frac{4}{3\sqrt{2}} s_{11} s_{12} \sigma + \frac{1}{3} s_{11}^{2} (1 - 2\sigma) \right] C_{144} + \left. \left. \left(-\frac{2}{3} s_{12}^{2} - \frac{4}{3\sqrt{2}} s_{11} s_{12} (1 - \sigma) - \frac{2}{3} s_{11}^{2} (1 + 4\sigma) \right] C_{166} \right\} \alpha_{1} \qquad (19)$$

Throughout α_1 is the strain in the direction of the stress, [111]

is the Poisson ratio - α_2/α_1 where α_2 is the strain in any direction perpendicular to the [111] direction.

In addition

$$s_{11} = \frac{1}{N} \cdot \frac{1}{3\sqrt{2}} \quad (c_{11} - c_{12} - 2c_{44})$$
 (19a)

$$s_{12} = -\frac{1}{N} \cdot \frac{1}{12} (C_{11} + 5C_{12} + 4C_{44} + R)$$
 (19b)

where

$$N = \left\{ \frac{1}{144} \left(C_{11} + 5C_{12} + 4C_{44} + R \right)^{2} + \frac{1}{18} \left(C_{11} - C_{12} - 2C_{44} \right)^{2} \right\}^{\frac{1}{2}} (19c)$$

$$R = \left\{ (C_{11} + 5C_{12} + 4C_{44})^2 + \frac{1}{8} (C_{11} - C_{12} - 2C_{44})^2 \right\}^{\frac{1}{2}}$$
 (19d)

(B) Under hydrostatic pressure*

For compressional wave in [100]

$$\rho_{o}V_{1}^{2} = C_{11} + \left\{ c_{11}^{\theta} + 2c_{12}^{\theta} + 4c_{11} + c_{111} + 2c_{112} \right\} \alpha \tag{20}$$

For compressional wave in [110]

$$\rho_{o}V_{2}^{2} = \frac{1}{2} (C_{11} + C_{12} + 2C_{44}) + \left\{ c_{11}^{\theta} + 2c_{12}^{\theta} + 2(C_{11} + C_{12} + 2C_{44}) + (C_{111} + 2C_{112}) - \frac{1}{2} (C_{111} - C_{123}) + C_{144} + 2C_{166} \right\} \alpha$$
 (21)

For shear wave in [100] polarized in direction [100]

$$\rho_0 V_3^2 = C_{44} + \left\{ C_{11}^{\theta} + 2C_{12}^{\theta} + 4C_{44} + C_{144} + 2C_{166} \right\} \alpha \tag{22}$$

For shear wave in [110] polarized in [110]

$$\rho_{o}V_{4}^{2} = \frac{1}{2} (c_{11} - c_{12}) + \left\{ c_{11}^{\theta} + 2c_{12}^{\theta} + 2(c_{11} - c_{12}) + \frac{1}{2}(c_{111} - c_{123}) \right\} \alpha \qquad (23)$$

For shear wave in [110] polarized in [001]

$$\rho_{0}V_{5}^{2} = C_{44} + \left\{ C_{11}^{\theta} + 2C_{12}^{\theta} + 4C_{44} + C_{144} + 2C_{166} \right\} \alpha \qquad (24)$$

^{*}Bhagavantam and Chelam 11 obtained expressions for the effective elastic constants which were different from those obtained by Birch. 9 Two points in B & C's derivation are subject to question. After corrections were made on them 12, B & C's expressions agree with Birch's.

(C) Under uniaxial compression in [110] direction 13,5.

For compressional wave in [001]

$$\rho_{0}v^{2} = C_{11} + \left\{-4\sigma_{001} C_{11} - \sigma_{001} C_{111} + (1 - \sigma_{110}) C_{112}\right\} \alpha_{1}$$
 (25)

For shear wave in [110] polarized in [110]

$$\rho_{0}V^{2} = \frac{1}{2}(c_{11} - c_{12}) + \left\{ (1 - \sigma_{110})(c_{11} - c_{12}) + \frac{1 - \sigma_{110}}{4} c_{111} - \frac{1 - \sigma_{110} + 2\sigma_{001}}{4} c_{112} + \frac{\sigma_{001}}{2} c_{123} \right\} \quad \alpha_{1}$$
 (26)

where α_1 is the strain in the direction of the stress, [110] σ_{001} and σ_{110} are the Poisson ratios for strains in [001]

and $[1\overline{1}0]$ directions respectively under a stress in [110]

direction. Explicit expressions for these quantities follow:

$$\sigma_{001} = \frac{4c_{12}^{\theta} c_{44}^{\theta}}{c_{11}^{\theta}(c_{11}^{\theta} + c_{12}^{\theta} + 2c_{44}^{\theta}) - 2 (c_{12}^{\theta})^{2}}$$
(27a)

$$\sigma_{110} = \frac{c_{11}^{\theta}(c_{11}^{\theta} + c_{12}^{\theta} - 2c_{44}^{\theta}) - 2(c_{12}^{\theta})^{2}}{c_{11}^{\theta}(c_{11}^{\theta} + c_{12}^{\theta} + 2c_{44}^{\theta}) - 2(c_{12}^{\theta})^{2}}$$
(27b)

By measuring the velocities of sound wave under stress, one can evaluate the coefficients of α or α_1 in equations 14 to 26 and solve for the third order elastic constants.

III. MATERIALS AND APPARATUS

NaCl and KCl single crystals in the form of 1" cubes and with faces oriented approximately in the 111, $1\overline{1}0$, and $\overline{1}\overline{1}2$ crystallographic directions were supplied by the Harshaw Chemical Co. The orientation of the crystals was checked by the Laue back reflection technique and the faces of the crystals were then ground to within $\pm 1/2^{\circ}$ of the exact orientation. After one face was oriented, the opposite face was then ground parallel to the first one to within .00003 inches. The dimensions of the specimen were measured with a supermicrometer (Pratt and Whitney) with a precision of 10 microinches.

10 Mc compressional and shear waves were generated respectively by 3/8" X-cut and Y-cut quartz transducers with an active circular area of 1/4" in diameter. The transducers were bonded to the specimen by phenyl salicylate ("salol").

Velocity measurements were made with a pulsed ultrasonic interferometer 14 constructed by A. D. Colvin 15. A brief description of this apparatus is given below:

Two pulses with a flat top of duration of 1 µs are gated out from a 10 Mc continuous sinusoidal wave. The time separation between the two pulses is variable from 3 to 10 µs on one range and 4 to 40 on another range. The pulse height of the second pulse can be adjusted from 0.5 to 1.0 as large as the first one. The echoes of the pulses are picked up with the same transducer and displayed on an oscilloscope. For the appropriate time

separation and ratio of pulse height, cancellation between the second echo of the first pulse and the first echo of the second pulse occurs at discrete frequencies. From the values of these frequencies nearest to the resonant frequency of the quartz transducer one can obtain the acoustic velocities 15. According to the procedure of Williams and Lamb 14, 15 one includes by an iterative procedure a correction for the phase change arising at the quartz-specimen interface. Additional corrections for changes in transit path because of stress and temperature are also included.

The velocities measured in the room temperature range were normalized to 25°C by the following equation:

$$V = V_T - \alpha_{vel} (T - 25)$$
 (28)

where $\alpha_{\rm vel}$ was the slope of the velocity vs temperature graph determined in the preliminary measurements for various modes in the room temperature range under atmospheric pressure.

A uniaxial compression was applied to the sample through a cylindrical movable piston in a cylinder made of hard steel. The surfaces of the piston and the bottom of cylinder between which the samples were compressed were carefully surfaced and kept parallel. The stress was applied to the piston through a hand-operated mechanical press. The cage of the press was surrounded by foam insulators to reduce the temperature fluctuation and a Cu-constantan thermocouple together with a Reeds and Northrup K-3 potentiometer were used to measure the temperature to .01°C.

The strain in the direction of the applied stress was measured with SR-4 strain gauges of type A-7 (Baldwin-Lima-Hamilton Corp.). Two pairs of strain

gauges were bonded on the opposite $\{110\}$ faces of the specimens. The two gauges on the same side were connected in series to give an average strain of that side. The reading of the strain on both sides were averaged to give the average strain of the specimen. In a typical run the difference between the strains on both sides was less than 10% for a maximum strain of 70 x 10^{-6} . Each pair of the strain gauges on the opposite faces of the sample form an arm of the two AC bridges in the two-channel recorder.

A dummy sample with the same type of strain gauges and the same connections was used as a control. Each pair of strain gauges on this dummy forms the other arm in an AC bridge and balances the corresponding pair of gauges on the test specimen. The dummy sample was kept at the same temperature as the specimen to eliminate the effect of temperature change on the reading of the strain.

IV. MEASUREMENTS

The temperature dependence of the velocities for various modes in NaCl and KCl obtained in preliminary measurements together with the values of velocity at T=25°C are listed in Table I. In the correction for the thermal expansion, the following coefficients of linear thermal expansion obtained from Henglein's measurements 16 were used:

NaC1

KC1

$$\frac{115}{3} \times 10^{-6} \text{ deg}^{-1} \text{ C}$$

$$\frac{110}{3} \times 10^{-6} \text{ deg}^{-1} \text{ C}$$

NaCl and KCl Together with the Values of Velocity.

(All values are at 25°C).

NaCl $\rho_0 = 2.162 \text{ g/cm}^3$

Direction	Direction	Slope of	Volenten
of Propagation	of Polarization	vel. vs. temp. (10 cm/µs/deg C)	(cm/µs)
111	111	-586	.44163
110	110	-827	.45058
110	110	-1477	.29043
110	001	-177	.24298
1 1 2	<u>11</u> 2	-903	.45171
112	111	-988	. 27355
112	110	-659	.25970
кс1	$\rho_{0} = 1.986$ g.	/cm ³	
111	111	-517	.36679
111	110	-1116	.25977
111	<u>11</u> 2	-1122	.25941
110	110	-834	.39014
110	110	-1453	.29106
110	001	-100	.17828
1 12	<u>11</u> 2	-1045	.39809
11 2	111	-805	.24656
ī ī2	110	-701	.22408

The adiabatic second order elastic constants at 25°C are determined from the $\rho_0^{\ 2}$ of the pure modes using the method of least squares. Their values are shown in Table II.

TABLE II

Adiabatic Second Order Elastic Constants of NaCl and KCl Crystals at 25°C (in units of 10 dynes/cm2)

	c_{11}	c_{12}	Сцц
NaC1	.4934	.1293	.1278
KC1	.4076	.0705	.0632

Except C_{12} of NaCl, these values agree with Lazarus' values to within half a percent. For C_{12} the difference is about 6%.

The KCl sample was compressed to a strain of 75×10^{-6} during the velocity measurement, the load was next reduced to the weight of the piston and then increased again. After a strain of about 90x10⁻⁶ drastic deformation occurred, and the calculated velocity drops as no account was taken of the change of the path length with plastic deformation. After the specimen was unloaded, the residual plastic strain was 45×10^{-9} . The strain was then recalculated excluding the permanent set, and the thickness remeasured after the transducers were removed. The p V as function of the recalculated strain is shown on the same graph (curve C). The weighted average of the slope before the plastic deformation is .3384 with a standard deviation σ of .0105. The slope after the plastic deformation is .3025. Since this value is beyond the lower 3σ limit, .3069, the difference in the slope before and after the plastic deformation appears to be significant. The effect is probably caused by the dislocations generated in plastic deformation. The effect of dislocations on the third order elastic constants has also been observed by Hikata et al in the harmonic generation of ultrasonic waves in aluminum.

It is tempting to conclude that the lower of $\rho_0 V^2$ curve by plastic deformation is also a dislocation effect but some systematic error could also have been introduced in the length measurement after removing the transducer and bonding material.

A summary of the slopes of $\rho_0 V^2$ vs $(-\alpha_1)$ graphs for various modes of propagation in NaCl and KCl under uniaxial compression in [111] direction is shown in Table III. For the uniaxial compression in [110], the results

for NaCl are shown in Table IV; no measurements were made on KCl under such a compression.

Lazarus has measured the velocities of sound waves in NaCl and KCl under hydrostatic pressure. From his data 6 , the quantity $\rho_0^{~~2}$ can be calculated and plotted against the strain (- α). The slopes of $\rho_0^{~~2}$ vs (- α) thus obtained are listed in Table V.

TABLE III Slope of $\rho_0^{\ V}$ vs (- α_1) graph under uniaxial compression 11 [111]

		1_	Slope of ρ V^2 vs $(-\alpha_1)$						
	Mod	ie	$(10^{12} \text{ dynes/cm}^2)$						
	Direction of	Direction of		C1	КС	1			
_	Propagation	Polarization	Measured Values	Weighted Average	Measured Values	Weighted Average			
v ₂₂	110	110	.4965*	.4965 <u>+</u> .0091	.4926 .3938 _* .4874	.4485 <u>+</u> .0231			
v _{2t1}	110	110	.6839 .6505	.6558 <u>+</u> .0087	.3143 (R11) .3645 (R12 Up) .3281 (R12 Dow .3442 (R13 Up) .3025 (R13 Dow	m)			
v _{2t2}	110	001	.3741 .3698	.3724 <u>+</u> .0029	.1830	.1830			
v ₃₂	112	110	.1792 .1641 .1538	.1736 <u>+</u> .0049	.1231	.1231 <u>+</u> .0023			
V ₃₃	112	112	.3137 [*] .3420	.3234 <u>+</u> .0067	. 4367	.4367 <u>+</u> .0048			
v ₃₁	112	111	.9482 .8537	.8706 <u>+</u> .0303	.3354	.3354 <u>+</u> .0032			

^{*}Velocity measurements were made with cancellation between the third echo of the first pulse against the first echo of the second pulse in order to obtain sharper cancellation.

TABLE IV Slope of $\rho_0 V$ vs (- α_1) graph for NaC1 under uniaxial compression // [110]

Mode			Slope of p ₀ V v (10 ¹² dy	Slope of ρ_0^2 vs $(-\alpha_1)$ graph $(10^{12} \text{ dynes/cm}^2)$				
<u>.</u>	Direction of Propagation	Direction of Polarization	Measured Values	Weighted Average	-			
V' 33	3 001	001	-1.627 -1.467	-1.564 <u>+</u> .053				
V'2t	110	110	+1.338 1.068 1.371 1.199	+1.218 + .052				

TABLE V Slope of ρ_0^2 vs (- α) graph under hydrostatic pressure (Calculated from Lazarus' data)

Мо	ode	Slope of $\rho_0 V^2$ vs $(-\alpha)$ graph $(10^{12} \text{ dynes/cm}^2)$				
of	Direction of Polarization	NaC1	KC1			
v ₁ 100	100	+7.2838 + .0730	+5.1973 <u>+</u> .0514			
v ₂ 110	110	+3.7832 ± .0813	+2.5786 ± .0417			
v ₃ 100	1 100	1597 ± .0011	$4195 \pm .0020$			
V ₄ 110	110	+2.8361 <u>+</u> .0093	$+2.4683 \pm .0134$			
v ₅ 110	001	1956*	4325 <u>+</u> .0025			
of Propagation V ₁ 100 V ₂ 110 V ₃ 100 V ₄ 110	of Polarization 100 110 1 100 110	+7.2838 + .0730 +3.7832 ± .0813 1597 ± .0011 +2.8361 ± .0093	+5.1973 ± .0514 +2.5786 ± .0417 4195 ± .0020 +2.4683 ± .0134			

 $^{^\}star$ From the first two measurements.

V. RESULTS AND DISCUSSION

A. The Linear Combinations of The Third Order Elastic Constants.

TABLE VI

Values of $s_{11}^{2},~2s_{11}~s_{12},~s_{12}^{2}$ and the Poisson ratios $\sigma,~\sigma_{001},$ and σ_{110}

			Expressions	Calculated NaC1	Value KC1
	s ₁₁			.00843	.06895
	2s ₁₁ s ₁₂		(19a) to (19d)	18287	50674
	s ₁₂			.99157	.93105
	Direction of Stress	Direction of Strain			
σ	111	1111	$\frac{c_{11}^{\theta} + 2c_{12}^{\theta} - 2c_{44}^{\theta}}{2(c_{11}^{\theta} + 2c_{12}^{\theta} + c_{44}^{\theta})}$.271	.337
σ	110	110	$\frac{c_{11}^{\theta}(c_{11}^{\theta}+c_{12}^{\theta}-2c_{44}^{\theta})-2c_{44}^{\theta})-2c_{44}^{\theta}}{c_{11}^{\theta}(c_{11}^{\theta}+c_{12}^{\theta}+2c_{44}^{\theta})-2c_{44}^{\theta})}$	$\frac{6^{2}}{12}$.155	.068
σ ₀₀₁	110	001	$\frac{4c_{12}^{f} c_{44}^{\theta}}{c_{11}^{\theta}(c_{11}^{\theta}+c_{12}^{\theta}+2c_{44}^{\theta})-2c_{44}^{\theta})}$.357	.554

TABLE VII $\label{eq:combinations} \mbox{Linear Combinations of C_{ijk} for NaCl }$

Under [111] compression:

	$C_{111} + 2C_{112}$	$c_{111} - c_{123}$	C ₄₅₆	C ₁₄₄	$C_{166} =$	Slope-2nd Order T	erms
v ₂₂ :	1526	+.0763	0	1526	+1.3895	+.0204 <u>+</u> .0110	(29)
v _{2t1}	: 0	0763	0	0	0	+.7670 <u>+</u> .0091	(30)
V _{2t2}	: 0	0	+.8474	1526	3053	+.3421 <u>+</u> .0033	(31)
٧ ₃₂ :	0	0254	+.5649	6667	+.3614	+.0154 <u>+</u> .0056	(32)
v ₃₃ :	1513	+.0687	0707	1701	+1.4350	1458 <u>+</u> .0112	(33)
٧ ₃₁ :	0013	0432	+.3531	+.5318	7122	+1.1027 <u>+</u> .0321	(34)

Under [110] compression:

	$\frac{c_{111}}{c_{111}}$	$\frac{c_{112}}{}$	C ₁₂₃	C ₄₅₆	C ₁₄₄	C ₁₆₆	=	Slope-2nd Order 7	Cerms
v' ₃₃ :	+.1551	6427	0	0	0	0		$-1.869 \pm .053$	(35)
V'2t1:	1607	+.2382	0775	0	0	0		$+1.452 \pm .052$	(36)

Under hydrostatic pressure (calculated from Lazarus' data)

	$C_{111} + 2C_{112}$	$C_{111} - C_{123}$	C144	C ₁₆₆	=	Slope-2nd Order To	erms
٧ ₁ :	-1	0	0	0		+9.9668 <u>+</u> .0730	(37)
v ₂ :	-1	$\frac{1}{2}$	-1	-2		$+6.2460 \pm .0813$	(38)
v ₃ :	0	0	-1	-2		+1.0608 <u>+</u> .0011	(39)
v ₄ :	0	$-\frac{1}{2}$	0	0		+4.2738 <u>+</u> .0093	(40)
٧ ₅ :	0	0	-1	-2		+1.025	(41)

The above equations are to be read horizontally, e.g.,

for V_{2t2} , .8474C₄₅₆ -.1526C₁₄₄ -.3053C₁₆₆ = .3421

Under [111] compression

	$c_{111} + 2c_{112}$	$c_{111} - c_{123}$	C ₄₅₆	C ₁₄₄	C ₁₆₆	= Slope-2nd Order Terms
v ₂₂ :	1084	+.0542	0	1084	+1.5664	+.0405 <u>+</u> .0231 (29')
v _{2t1} :	0	0542	0	0	0	+.3978 <u>+</u> .0076 (30')
٧ _{2t2} :	0	0	+.8916	1084	2168	+.1540 (31')
٧ ₃₂ :	0	0181	+.5944	6667	+.4499	0096 <u>+</u> .0023 (32')
v ₃₃ :	1009	+.0350	1925	1430	+1.5707	+.0688 <u>+</u> .0048 (33')
٧ ₃₁ :	0075	0170	+.4897	+.5929	6710	+.4722 <u>+</u> .0032 (34')

Under hydrostatic pressure (calculated from Lazarus' data)

	$c_{111} + 2c_{112}$	$c_{111} - c_{123}$	C144	C ₁₆₆	= Slope-2nd Order Terms
٧ ₁ :	-1	0	0	0	+7.3477 <u>+</u> .0514 (37')
v ₂ :	-1	$\frac{1}{2}$	-1	-2	+4.3079 <u>+</u> .0417 (38')
v ₃ :	0	0	-1	-2	+ .3535 <u>+</u> .0020 (39')
v ₄ :	0	$-\frac{1}{2}$	0	0	+3.6625 ± .0134 (40')
v ₅ :	0	0	-1	-2	+ .3405 <u>+</u> .0025 (41')

Before solving these equations, we shall check their internal consistency.

B. Internal Check Among the Measurements under [111] Compression:

From the coefficients of $(-\alpha_1)$ in the equations (14) to (19), one can show that (33) and (34) can be expressed in terms of (29) to (32) as:

$$(33) = (29) \times s_{12}^{2} + (30) \times (s_{11}^{2} - \frac{s_{11} s_{12}}{\sqrt{2}}) + (31) \times (s_{11}^{2} + \frac{2s_{11}s_{12}}{\sqrt{2}}) + (32) \times (-s_{11}^{2} - \frac{1}{\sqrt{2}} s_{11}s_{12})$$
(42)

$$(34) = (29) \times s_{11}^{2} + (30) \times (s_{12}^{2} + \frac{s_{11}s_{12}}{\sqrt{2}})$$

$$= (31) \times (s_{12}^{2} - \frac{2s_{11}s_{12}}{\sqrt{2}}) + (32) \times (-s_{12}^{2} + \frac{1}{\sqrt{2}}s_{11}s_{12})$$

$$(43)$$

Hence there are two internal checks. Same relationships also hold for equations (29') to (34') for KC1.

For the measurements on NaCl, the right side of (42) is $.0341 \pm .0103$ while the left side is $-.1458 \pm .0067$; the right side of (43) is $1.076 \pm .0166$ while the left side is $1.103 \pm .0303$. For the measurements on KCl, the right side of (42) is $.0908 \pm .0309$ while the left side is $.0688 \pm .0048$; the right side of (43) is $.5111 \pm .0100$ while the left side is $.4722 \pm .0032$.

It can be seen from these internal checks that the measurements on KCl under [111] compression are reasonably consistent. The difference is within the limit of three times the standard deviation. For NaCl one of the internal checks (42) is poorly satisfied and it is thought that the blame lies with the V₂₂ measurement. In this measurement the output impedence of the gate circuit and the cable were improperly matched and hence the input signal to the transducer was very small. This mismatching was remedied for the other subsequent

measurements and a considerably larger S/N ratio was obtained which enabled more accurate measurements. The equation (43) again is satisfied quite well.

C. Internal Check Among the Measurements Under Hydrostatic Pressure

Among the five equations (37) to (41), only three are linearly independent. Hence there are two internal checks. It can be shown that

$$(38) = (37) - (40) + \frac{(39) \text{ or}}{(41)}$$
 (44)

Same relationship also holds for eqs. (37') to (41') for KCl.

From Lazarus' data for NaCl (Table VII), the right side of (44) using (39) is $6.754 \pm .083$, or using (41) is 6.719, while the left side is $6.246 \pm .081$; for KCl (Table VIII), the right side using (39) is $4.039 \pm .066$, or using (41) is $4.026 \pm .067$, while the left side is $4.308 \pm .042$. The discrepancies are all within the limit of three times the standard deviation.

D. Determination of the Five Third Order Elastic Constants

From the measurements under [111] compression and those under hydrostatic pressure by Lazarus, five third order elastic constants can be determined. A preliminary question is how to weight these two sets of equations.

For NaCl the averaged probable error in the data for the [111] compression (Table III) is about 1/4 of that in the data for the hydrostatic compression (Table IV). For KCl it is about 1/3. Hence in solving for the elastic constants, we shall weight the set of equations for NaCl under [111] compression by 4 against the set under the hydrostatic pressure. For KCl, the corresponding set will be weighted by 3.

The values of the five third order elastic constants determine from these weighted equations using the method of least squares are shown in Table IX.

TABLE IX

Values of the Five Third Order Elastic Constants for NaCl and KCl at 25°C (10^{-12} dynes/cm)

	$c_{111} + c_{112}$	$c_{111} - c_{123}$	C ₄₅₆	6 <u>144</u>	C ₁₆₆ _
NaC1	-9.91	-9.10	.271	.257	611
	<u>+</u> .04	<u>+</u> .08	<u>+</u> .014	<u>+</u> .016	<u>+</u> .007
KC1	-7.44	-7.15	.118	.127	245
	<u>+</u> .01	<u>+</u> .02	<u>+</u> .004	+.005	<u>+</u> .002

For the purpose of comparison, calculations in which the set of equations under [111] compression was weighted by 1 and 10 were also made. The largest shifts were about 8% in C_{111} - C_{123} for NaCl and 18% in C_{144} for KCl. For the other constants, the shifts were less than 6%.

From the values of $C_{4,56}$ and C_{144} , it can be seen that one of the Cauchy relation for third order constants, $C_{4,56} = C_{144}$, is satisfied to within the probable error for both NaCl and KCl crystals at room temperature.

E. Evaluation of the Six Third Order Elastic Constants

Since from the measurements under the [111] and hydrostatic compressions only five third order elastic constants can be determined, an effort was made to obtain other independent equations by making measurements under a unixial compression applied in the [110] direction.

Unfortunately, when such a compression is applied, the resolved shear stress in the easy slip direction of dislocations in the slip planes does not vanish, and plastic deformation sets in easily and affects the measurements. Moreover, as it can be seen from the equations (35) and (36) for the [110] compression that the numbers on the right side are much larger than the coefficients on the left side. A slight fluctuation in the measurement effects the final result of the six third order elastic constants very much. For example, on the right side of equation (36) a change from 1.45 to 1.30 (which is within the limit of three times the standard deviation for measurements under this compression) causes the resulting C_{112} changing from 0.29 to-0.50 and the resulting C_{123} from -.413 to +.014. Hence the data obtained from the [110] compression were not used in the evaluation of the third order elastic constants. However, they can serve as a check to the evaluation by another method as will be described below.

Since the Cauchy relation $C_{456} = C_{144}$ is satisfied to within the probable error we shall assume the validity of the other two Cauchy relations $C_{123} = C_{456}$ and $C_{112} = C_{166}$, although this assumption is open to some question because, as Nran'yan has shown, only the relation $C_{456} = C_{144}$

can be expected to hold at all temperatures even for a central force model. The other two equalities hold only at $0^{\circ}K$. However, we shall use these relations to estimate the values of C_{111} , C_{112} , and C_{123} at room temperature. From the results in Table IX,

(For NaC1) (For KC1)
$$C_{111} + 2C_{112} = -9.91 -7.44$$

$$C_{111} - C_{123} = -9.10 -7.15$$
(46)

If we assume

$$C_{123} = \frac{1}{2}(C_{456} + C_{144}) = .264$$
 .123 (47)

$$C_{112} = C_{166} = -.611 -.245$$
 (48)

then we can check the consistency of these equations.

The relation relating these four equations is

$$(45) - 2 \times (48) = (46) + (47) \tag{49}$$

For NaCl, the left side of (49) is -8.69 while the right side is -8.84; for KCl, the left side is -6.95 while the right side is -7.03. Hence the introduction of the other two Cauchy relations does not cause appreciable inconsistency among these equations. Using the method of least squares, one can obtain the estimated values of C_{111} , C_{112} , and C_{123} from the four equations (45) to (48). The results are shown parenthetically in Table X.

Using these extimated values, one can check the results obtained from the [110] compression in NaCl. For V_{33}^{\prime} one obtains -1.00 for the left side of equation (35) while the value on the right side obtained through the experiment is -1.87. For V_{2t1}^{\prime} , one obtains 1.25 for the left side of equation (36) while the value on the right side is 1.45. Although the value for V_{2t1}^{\prime} are rather close, the discrepancy in V_{33}^{\prime} is quite large.

This indicates that the internal consistency in the measurements under the [110] compression is poor. This may be caused by the dislocation contribution to the third order elastic constants and also the small range of strain which reduced the accuracy of the measurements.

G. Comparison with Theory

While this experiment was underway, A.A. Nran'yan¹⁸ published values of the third order elastic constants of NaCl - type alkali halide crystals. He used the Born-Mayer model in which the potential energy between two particles was represented by the following expression:

$$\phi_{\mu\nu} R_{\mu\nu}^{mo} = (\pm)_{\mu\nu} \frac{e}{R_{\mu\nu}^{mo}} + B_{\mu\nu} e^{-\frac{R_{\mu\nu}^{mo}}{b_{\mu\nu}}}$$

Where $R_{\mu\nu}^{mo}$ is the distance between the equilibrium positions of the μ^{th} particle in the m^{th} cell and the ν^{th} particle in the 0^{th} cell in the deformed lattice

e is the electronic charge

 $b_{\mbox{\tiny LIV}}$ and $B_{\mbox{\tiny LIV}}$ are two constants describing the repulsion and

$$(+)_{\mu\nu}$$
 = + when $\mu = \nu$
- when $\mu \neq \nu$

The first term represents the contribution from the Coulomb interaction and the second represents the repulsion of their electron shells.

The theoretical values of the third order elastic constants and their linear combinations at room temperature are listed in Table X together with the present experimentally determined values.

TABLE X Comparison between Experimental and Theoretical Values of C_{ijk} and Their Combinations at 25°C (In Brugger's definition of C_{ijk} and in units of 10^{12} dynes/cm²)

	NaC1		KC1		
	Ежр.	Th.	Exp.	Th.	
c ₁₁₁	(-8.80)	-5.45	(-7.01)	-5.07	
C ₁₁₂	(571)	688	(244)	458	
C ₁₂₃	(.284)	.269	(.133)	.148	
$c_{111} + 2c_{112}$	-9.91	-6.83	-7.44	-5.99	
$c_{111} - c_{123}$	-9.10	-5.72	-7.15	-5.22	
C ₄₅₆	.271	.325	.118	.207	
C ₁₄₄	.257	.325	.127	.207	
C ₁₆₆	611	63	245	40	

Parenthetical values are the ones estimated by assuming the Cauchy relations.

It is seen that the sign and the order of magnitude of the theoretically predicted values agree with experiment although quantitative agreement is lacking.

VI CONCLUSIONS

The relations between the velocities of sound waves propagating along the $[1\bar{1}0]$ and $[\bar{1}\bar{1}2]$ directions in a cubic lattice of high symmetry under a unixial compression applied in [111] direction were derived. The velocities of ultrasonic waves were measured at room temperature as functions of the strain using the pulsed ultrasonic interference technique. From the measurements under the [111] compression and those under hydrostatic pressure, the values of five third order elastic constants of NaCl and KCl at room temperature were obtained. It is seen that the Cauchy relation $C_{456} = C_{144}$ is satisfied to within the probable error for both NaCl and KCl single crystals at toom temperature. By assuming the validity of the other two Cauchy relations, one can estimate the values of C_{111} , C_{112} , and C_{123} . The theoretical values predicted by A.A. Nran'yan were compared with the experiment. Although the sign and order of magnitude agree quite well, some discrepancies exist between the values.

ACKNOWLEDGMENTS

H. B. Huntington for suggesting the problem and for his many enlightening discussions and guidance throughout the course of this work. The author is also indebted to Professor J. L. Katz for the use of the x-ray equipment and the IBM 1620 computer, and to Professor R. H. Trathen for his helpful advice in the measurement of strain and the use of the equipment.

APPENDIX

Adiabatic and Isothermal

Second Order Elastic Constants

For infinitesimal strains, it has been shown 19 that the differences between the adiabatic and isothermal elastic constants are:

$$c_{11}^{\sigma} - c_{11}^{\theta} = c_{12}^{\sigma} - c_{12}^{\theta} = \frac{\alpha^{2}(C_{11} + 2C_{12})^{2}T}{\rho C_{\mathbf{v}}}$$

$$c_{44}^{\sigma} - c_{44}^{\theta} = 0$$

where α is the linear thermal expansion coefficient, T is the absolute temperature and $C_{\bf v}$ is the specific heat at constant volume. For NaCl at T = 300°K, α = 38.3 x 10⁻⁶ /deg C, C_{11} + 2 C_{12} = .752 x 10¹² dynes/cm² and ρ = 2.162 g/cm³. With $C_{\bf v}$ = .811 J/g deg C, one obtains C_{11}^{σ} = C_{11}^{θ} = .0142 x 10¹² dynes/cm². From the values of $C_{\bf ij}^{\sigma}$ in Table II, one obtains C_{11}^{θ} = .4792, C_{12}^{θ} = .1151 (10¹² dynes/cm²). For KCl at T = 300°K, α = 36.7 x 10⁻⁶/deg C, C_{11} + 2 C_{12} = .549 x 10¹² dynes/cm² and ρ = 1.986 g/cm³. With $C_{\bf v}$ = .644 J/g deg C, one obtains C_{11}^{σ} - C_{11}^{θ} = .0095 x 10¹² dynes/cm². From the values of $C_{\bf ij}^{\sigma}$ in Table II, one obtains C_{11}^{θ} = .3981, C_{12}^{θ} = .0610 (10¹² dynes/cm²)

LIST OF TABLES

Page

Table	I	Temperature Dependence of Velocity of Sound Waves in NaCl and KCl together with the Values of Velocity
Table	11	Adiabatic Second Order Elastic Constants of NaCl and KCl
Table	III	Slope of ρ V vs $(-\alpha_1)$ Graph (Under [111] Compression)
Table	IV	Slope of ρ_0^2 vs $(-\alpha_1)$ Graph (Under [110] Compression)
m_L 1_	17	Slope of ρ_0^2 vs (- α) Graph
Table	V	(Under Hydrostatic Pressure)
Table	VI	Values of s_{11} , $2s_{11}s_{12}$, s_{12} , and the Poisson Ratios σ , σ_{001} , σ_{110}
Table	VII	Linear Combinations of C
Table	VIII	Linear Combination of C _{ijk} KC1
Table	IX	Values of Five Third Order Elastic Constants of NaCl and KCl at Room Temperature
Table	x	Comparison between Experimental and Theoretical Values of $C_{\mbox{ijk}}$ and their Combination at Room Temperature

FIGURE CAPTION

- Fig. 1 ρ₀V vs strain for shear wave in NaCl under stress [111].
 Curve (A) for wave propagating in [112] and polarized in [111].
 Curve (B) for wave propagating in [110] and polarized in [001].
 Circles measured during increasing stress; crosses measured during decreasing stress.
- Fig. 2 $\rho_0 V$ vs strain for shear wave in KC1 under stress [111]. Curve (A) for wave propagating in [$\overline{11}2$] and polarized in [111]. Curve (B) for wave propagating in [$\overline{11}0$] and polarized in [001]. Circles measured during increasing stress; crosses measured during decreasing stress.
- Fig. 3 ρ V vs strain for shear wave in KCl under stress [111] propagating in [110] and polarized in [110]. (A) Before plastic deformation.
 - Run 12 up; x Run 12 down; o Run 13 up
 - (B) After plastic deformation. Δ Run 13 down
 - (C) After plastic deformation (with the plastic strain excluded and using the thickness after the plastic deformation) ▲ Run 13 down.

LITERATURE CITED

- 1. M.A. Breazeale and D.O. Thompson, Appl. Phys. Letters 3, 77 (1963)
- 2. F.R. Rollins, Appl. Phys. Letters 2, 147 (1963)
- 3. J. Melngailis, A.A. Maradudin, and A. Seeger, Phys. Rev. 131, 1972 (1963)
- 4. D.S. Hughes and J.L.Kelly, Phys. Rev. 92, 1145 (1953)
- 5. T. Bateman, W.P. Mason, and H.J. McSkimin, J. of Appl. Phys. 32, 928 (1961)
- 6. D. Lazarus, Phys. Rev. <u>76</u>, 545 (1949)
- 7. R.A. Bartels, Office of Naval Research Technical Report No. 8 (1964)
- 8. K. Brugger, Phys. Rev. <u>133</u>, A1611 (1964)
- 9. F. Birch, Phys. Rev. 71, 809 (1947)
- 10. T.D. Murnaghan, Finite Deformation of an Elastic Solid (Wiley and Sons, New York 1951)
- 11. S. Bhagavatam and E.V. Chelam, Proc. Indian Acad. of Sciences 25A, 1 (1960)
- 12. Z.P. Chang, Ph.D. Thesis (Rensselaer Polytechnic Institute, Troy, N. Y. 1964)
- 13. A. Seeger and O. Buck, Z. Naturforschg 15a, 1056 (1960)
- 14. J. Williams and J. Lamb, J. of Acoust. Soc. Am. 30, 308 (1958)
- 15. A.D. Colvin, Master's Thesis (Rensselaer Polytechnic Institute, Troy, N. Y. 1959)
- F.A. Henglein, Zeitschrift fur Phys. Chem. 115, 91 (1925)
- 17. A. Hikata, B.B. Chick and C. Elbaum, Appl. Phys. Letters <u>3</u>, 195 (1963)
- A.A. Nran'yan, Soviet Physics Solid State <u>5</u>, 129 (1963);
 1361 (1964)
- 19. W.P. Mason, Piezoelectric Crystals and Their Application to Ultrasonics (Van Norstrand, Princeton, N. J. 1958)